

## The Anharmonic Temperature Factor for Crystals with the Hexagonal Wurtzite Structure and Its Inclusion in Models for Least-squares Refinement of Intensity Data

A. Fakineos,<sup>A</sup> A. W. Stevenson<sup>A,B</sup> and Z. Barnea<sup>A</sup>

<sup>A</sup> School of Physics, University of Melbourne, Parkville, Vic. 3052.

<sup>B</sup> Author to whom correspondence should be addressed.

### Abstract

The anharmonic temperature factor for binary compounds of the  $A^N B^{8-N}$  type possessing the wurtzite structure is derived as a perturbation expansion about the harmonic case. The terms in this expansion are obtained from combinations of spherical harmonics. The derivation utilizes group theory and follows the treatment of Von der Lage and Bethe (1947) and Nizzoli (1976). A set of constraints between the cubic anharmonic coefficients in the one-particle potential (OPP), which appear in the temperature factor, is then derived, enabling least-squares refinements to be carried out successfully. The use of the anharmonic temperature factor, with these constraints, is shown to result in a significant reduction in Hamilton's  $R$  factor for two extensive data sets.

### 1. Introduction

A generalized structure factor formalism has been developed by Dawson (1967*a*) for interpreting accurate X-ray and neutron diffraction data. One of the advantages of this formalism is that effects such as anharmonic thermal vibration and bonding are readily incorporated. It is with the first of these effects that this paper is primarily concerned. Bonding will be mentioned only briefly, since Moss (1977) has determined that bonding effects in wurtzite structures are small and they have been neglected in the analyses discussed here.

In Section 2 we derive an expression for the anharmonic temperature factor. The approach used differs from that of Mair and Barnea (1975) and Whiteley *et al.* (1978), who expanded the one-particle potential (OPP) as a power series in the atomic displacements from appropriate positions (Mair and Wilkins 1981) within the restrictions imposed by the local site symmetry. In the present paper we use a group theory approach, demonstrated by Nizzoli (1976) for zinc.

The final expression for the temperature factor, when included in the general structure factor, introduces six cubic anharmonic parameters (three for each atomic species, A and B). An attempt to refine the six parameters would result in severe correlation, both between these parameters themselves and with the other refined parameters. In Section 3 we derive approximate constraints which reduce the six anharmonic parameters to two (one for each atomic species), resulting in a model more amenable to least-squares refinement and producing more reliable parameter values.

Tests of the structure factor model are described briefly in Section 4 for two extensive X-ray intensity data sets for cadmium sulfide and cadmium selenide.

## 2. Anharmonic Temperature Factor

The point group for the hexagonal wurtzite structure is  $3m$ , which specifies the symmetry for the electron charge distribution at an atomic position. Of the two one-dimensional irreducible representations of this point group ( $A_1$  and  $A_2$ ), only  $A_1$  ensures the invariance of the charge under the operations of the group (see the character table on p. 58 of Bradley and Cracknell 1972). The angular dependence of the charge distribution  $\rho(\mathbf{r})$  can now be expanded using a set of hexagonal harmonics appropriate to  $A_1$  (combinations of spherical harmonics obtained from characteristic polynomials (CP)). The method of Von der Lage and Bethe (1947) is used in constructing this set from the CP.

By using the compatibility tables of Bradley and Cracknell (1972; p. 73), the number of linearly independent polynomials which can be constructed for each value of the angular momentum  $L$  can be ascertained. In this case there is one polynomial for  $L = 0, 1$  and  $2$ , and two for  $L = 3$ . A possible choice of CP, denoted by  $P_L$ , is

$$\begin{aligned} P_0 &= 1, & P_1 &= z, & P_2 &= z^2, \\ P_3^1 &= z^3, & P_3^2 &= (u-v)(u-w)(v-w). \end{aligned} \quad (1)$$

In the Miller-Bravais notation used in equations (1) any given vector can be expressed in terms of the basis vectors  $\mathbf{i}$ ,  $\mathbf{h}$ ,  $\mathbf{k}$  and  $\mathbf{l}$  as  $u\mathbf{i} + v\mathbf{h} + w\mathbf{k} + z\mathbf{l}$ , with  $w = -(u+v)$ . The basis vector  $\mathbf{l}$  is perpendicular to the basal plane and the other three are in the basal plane at angles of  $120^\circ$  to each other.

The hexagonal harmonics of each order can now be constructed from equations (1) by dividing the CP by  $r^L$  and imposing orthogonality conditions:

$$\begin{aligned} H_0(\mathbf{r}/r) &= 1, & H_1(\mathbf{r}/r) &= z/r, & H_2(\mathbf{r}/r) &= z^2/r^2 - \frac{1}{3}, \\ H_3^1(\mathbf{r}/r) &= z^3/r^3 - \frac{3}{5}z/r = z^3/r^3 - \frac{3}{5}H_1(\mathbf{r}/r), \\ H_3^2(\mathbf{r}/r) &= (u-v)(u-w)(v-w)/r^3, \end{aligned} \quad (2)$$

where  $r^2 = \frac{3}{2}(u^2 + v^2 + w^2) + z^2 = r_B^2 + z^2$ .

Following Nizzoli (1976),  $\rho(\mathbf{r})$  can be written as the sum of a spherical term and angular dependent contributions, whose form is the product of a radial function (Dawson 1967b) and one of the hexagonal harmonics in equations (2). The Fourier transforms of these terms represent the various contributions to the atomic scattering factor, where the transform of the spherical term includes the Hartree-Fock spherical atom scattering factor.

In order to obtain the anharmonic temperature factor we first construct the probability density function (PDF) for thermal motion in terms of the polynomials already obtained. The zero-order approximation for the PDF is taken to be a normal distribution (Johnson 1970) of the form

$$\bar{i}(\mathbf{r}) = N \exp\left[-\frac{1}{2}\{(r_B^2/\langle u_{11}^2 \rangle) + (z^2/\langle u_{33}^2 \rangle)\}\right],$$

where  $N$  is a normalization constant and  $\langle u_{11}^2 \rangle$  and  $\langle u_{33}^2 \rangle$  are the mean-square displacements in the basal plane and along the  $z$ -axis respectively. By using the table supplied by Johnson (1970), giving the number of unique coefficients in the

cumulant tensors which enter the generalized expansions of the PDF (for different orders (up to 5) and point groups), the number of independent terms for each order in the expansion can be ascertained. The expansion, to third order, is

$$t(\mathbf{r}) = \bar{t}(\mathbf{r})\{1 + B_1(u-v)(u-w)(v-w) + B_2 z r_B^2 + B_3 z^3\}, \quad (3)$$

where the single first-order term has been omitted. This omission is equivalent to making a Taylor expansion of the OPP about the positions defining the minima of that potential, in contrast to an expansion about the thermodynamic equilibrium positions, where a first-order term does occur (Mair and Wilkins 1981). Mair and Wilkins have shown that it is not possible to refine simultaneously both for the effect of the coefficient of the first-order term in the temperature factor and for the equilibrium position. Consequently, the first-order term must not occur in the expression for the temperature factor to be used in the least-squares refinement.

By normalizing the PDF in equation (3) and then, with the help of Gradshteyn and Ryzhik (1965), taking the Fourier transform, results in the following expression for the temperature factor:

$$\begin{aligned} T(s) = \bar{T}(s) \{ & 1 + j(4\pi/3a)^3 B_1 \langle u_{11}^2 \rangle^3 (i-h)(i-k)(h-k) \\ & + jB_2 \langle u_{11}^2 \rangle \langle u_{33}^2 \rangle s_z (2 - s_B^2 \langle u_{11}^2 \rangle) \\ & + jB_3 \langle u_{33}^2 \rangle^2 s_z (3 - s_z^2 \langle u_{33}^2 \rangle) \} \end{aligned} \quad (4)$$

where the harmonic temperature factor is given by

$$\bar{T}(s) = \exp[-2\pi^2 \{ l^2 \langle u_{33}^2 \rangle / c^2 + 2(i^2 + h^2 + k^2) \langle u_{11}^2 \rangle / 3a^2 \}]. \quad (5)$$

In equations (4) and (5)  $s = |s| = 2 \sin \theta / \lambda$ ,  $\theta$  being the Bragg angle and  $\lambda$  the wavelength of the incident radiation;  $j = (-1)^{\frac{1}{2}}$ ;  $a$  and  $c$  are the lattice constants;  $i, h, k$  and  $l$  are the Miller-Bravais indices of a plane,  $i = -(h+k)$ ;

$$s_z = 2\pi l / c \text{ and } s_B = (2\pi/a) \{ \frac{2}{3}(i^2 + h^2 + k^2) \}^{\frac{1}{2}}.$$

The high-temperature behaviour of  $T(s)$  can be determined by comparing equation (3), term by term, with the classical expression  $N \exp\{-v(\mathbf{r})/k_B T\}$ , where  $v(\mathbf{r})$  is the OPP,  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature. To third order,  $v(\mathbf{r})$  has the form

$$\begin{aligned} v(\mathbf{r}) = & \beta_{001} + \beta_{201} r^2 + \beta_{225} \frac{1}{2}(3z^2 - r^2) + \beta_{313} z r^2 \\ & + \beta_{332}(3x^2 - y^2)y + \beta_{337} \frac{1}{2}(5z^2 - 3r^2)z, \end{aligned} \quad (6)$$

where  $(x, y, z)$  form a cartesian coordinate system with the  $x$ -axis perpendicular to the mirror plane, and the coefficients  $\beta_{rst}$  follow the notation of Whiteley *et al.* (1978). The absence of the first-order term,  $\beta_{113}z$ , in equation (6) has been discussed in connection with equation (3). If the anharmonic distortions are small the comparison of the classical expression for  $t(\mathbf{r})$  and equation (3) gives

$$\begin{aligned} B_1 & \equiv -3\sqrt{3} \beta_{332} / 2k_B T, & \langle u_{11}^2 \rangle & \equiv k_B T / (2\beta_{201} - \beta_{225}), \\ B_2 & \equiv (3\beta_{337} - 2\beta_{313}) / 2k_B T, & \langle u_{33}^2 \rangle & \equiv k_B T / \{2(\beta_{201} + \beta_{225})\}, \\ B_3 & \equiv -(\beta_{313} + \beta_{337}) / k_B T, \end{aligned} \quad (7)$$

Substituting equations (7) into (4) and (5) gives

$$T(s) = \bar{T}(s) \left\{ 1 + j \left( \frac{4\pi}{3a(\beta_{225} - 2\beta_{201})} \right)^3 \sqrt{3} \beta_{332} (k_B T)^{2\frac{1}{2}} (i-h)(i-k)(h-k) \right. \\ \left. + \frac{j(3\beta_{337} - 2\beta_{313})k_B T \pi l [2 - 8\pi^2(i^2 + h^2 + k^2)k_B T / \{3a^2(2\beta_{201} - \beta_{225})\}]}{2c(2\beta_{201} - \beta_{225})(\beta_{201} + \beta_{225})} \right. \\ \left. + \frac{j(\beta_{313} + \beta_{337})k_B T \pi l [2k_B T \pi^2 l^2 / \{c^2(\beta_{201} + \beta_{225})\} - 3]}{2c(\beta_{201} + \beta_{225})^2} \right\}, \quad (8)$$

where

$$\bar{T}(s) = \exp \left\{ -2\pi^2 k_B T \left( \frac{l^2}{2c^2(\beta_{201} + \beta_{225})} + \frac{2(i^2 + h^2 + k^2)}{3a^2(2\beta_{201} - \beta_{225})} \right) \right\}. \quad (9)$$

Equations (8) and (9) can be shown to be equivalent to the expressions of Mair and Barnea (1975) and Whiteley *et al.* (1978). In particular, we have

$$2\beta_{201} - \beta_{225} = 8\pi^2 k_B T / B_{11}, \quad (10)$$

$$\beta_{201} + \beta_{225} = 4\pi^2 k_B T / B_{33}, \quad (11)$$

where  $B_{11}$  and  $B_{33}$  are the conventional hexagonal temperature parameters.

### 3. Constraints between Cubic Anharmonic Parameters

If the anharmonic temperature factor given by equations (8) and (9) is included in a model for least-squares refinement of intensity (or structure factor) data, ten parameters must be varied (i.e.  $\beta_{201}$ ,  $\beta_{225}$ ,  $\beta_{313}$ ,  $\beta_{332}$  and  $\beta_{337}$  for each atomic species). Such a refinement results in high correlations between the cubic anharmonic parameters themselves, as well as between these and other refined parameters. The resulting parameter values are unreliable and have high estimated standard deviations (e.s.d.). These high correlations are essentially independent of the quality of the data, but depend on the model being used and to some extent on the quantity of data (Geller 1961).

**Table 1.** Sign conventions for cubic anharmonic parameters for each atom in unit cell

Atom A(1) is at the origin				
Parameter	A(1)	Sign convention		
		A(2)	B(1)	B(2)
$\beta_{313}$	—	—	+	+
$\beta_{332}$	+	—	+	—
$\beta_{337}$	+	+	—	—

Whiteley *et al.* (1978), in carrying out a least-squares refinement of anharmonic intensity ratios, arbitrarily set all six cubic anharmonic parameters equal in magnitude. The sign conventions, for each of the four atoms in the unit cell, can be obtained by considering the relative orientations of the potential components. These sign conventions, which are relative, have been given by Whiteley *et al.* (1978) and are reproduced in Table 1 for convenience.

In an attempt to obtain more realistic relations between the cubic anharmonic parameters for a particular atomic species we make use of certain physical properties which impose restrictions on the form of the OPP. Initially the entire OPP in equation (6) is dealt with, but the use of the approximation  $B_{11} = B_{33}$  makes the treatment equivalent to starting with only cubic terms, i.e. the harmonic terms do not enter into the constraint equations when this approximation is made. The structure is treated as being ideal wurtzite, i.e. nearest neighbour atoms form a perfect tetrahedron. Such an approximation is reasonable for the cases of CdS and CdSe discussed in Section 4, where the  $c/a$  ratios deviate by approximately 0.6% and 0.1% from the ideal value of  $\sqrt{\frac{8}{3}}$  respectively. The equations and inequalities derived initially will apply to the A(1) atom and the results will subsequently be extended to the other atoms in the unit cell. Thus, by equating the OPP for such an atom for equal displacements along the  $c$ -axis bond and along any one of the other three bonds, the following equation is obtained:

$$9\beta_{313} - 4\sqrt{2}\beta_{332} + 4\beta_{337} = 0, \quad (12)$$

where we have assumed

$$\beta_{225} = 0. \quad (13)$$

**Table 2. Approximate relationships for cubic anharmonic parameters**  
The prime distinguishes between the anharmonic parameters for the two atomic species

Parameter	A(1)	A(2)	Relationship	B(1)	B(2)
$\beta_{313}$	0	0		0	0
$\beta_{332}$	$ \beta_{332} $	$- \beta_{332} $		$ \beta_{332} '$	$- \beta_{332} '$
$\beta_{337}$	$\sqrt{2} \beta_{332} $	$\sqrt{2} \beta_{332} $		$-\sqrt{2} \beta_{332} '$	$-\sqrt{2} \beta_{332} '$

**Table 3. Approximate relationships for cubic anharmonic parameters of Mair and Barnea (1975)**

Parameter	A(1)	A(2)	Relationship	B(1)	B(2)
$\beta_1$	$ \beta_1 $	$- \beta_1 $		$ \beta_1 '$	$- \beta_1 '$
$\beta_2$	$-\frac{1}{3}\sqrt{6} \beta_1 $	$-\frac{1}{3}\sqrt{6} \beta_1 $		$\frac{1}{3}\sqrt{6} \beta_1 '$	$\frac{1}{3}\sqrt{6} \beta_1 '$
$\beta_3$	$\frac{2}{3}\sqrt{6} \beta_1 $	$\frac{2}{3}\sqrt{6} \beta_1 $		$-\frac{2}{3}\sqrt{6} \beta_1 '$	$-\frac{2}{3}\sqrt{6} \beta_1 '$

Equation (13) implies that the conventional hexagonal temperature parameters,  $B_{11}$  and  $B_{33}$ , are equal (see equations 10 and 11). In the cases of CdS and CdSe the differences between  $B_{11}$  and  $B_{33}$  are approximately 3% and 1.5% respectively (these differences are the averages of those for the two atomic species in each case).

If the OPP in equation (6) is maximized along bonding directions and minimized along antibonding directions, and equation (13) is used, the following requirements are found:

$$3\beta_{313} + 2\sqrt{2}\beta_{332} - 2\beta_{337} = 0, \quad (14)$$

$$\beta_{313} - 4\sqrt{2}\beta_{332} - 14\beta_{337} < 0, \quad (15)$$

$$\beta_{313} + 6\beta_{337} > 0. \quad (16)$$

The antibonding directions used in the derivation of relations (14)–(16) refer to the directions of the three octahedral holes which, together with the tetrahedral hole centred on the *c*-axis, surround each atom.

By using relations (12), (14) and (16) it is possible to obtain  $\beta_{313}$ ,  $\beta_{332}$  and  $\beta_{337}$  in terms of a single parameter. The inequality (15) provides no new information, i.e. it can be obtained from relations (12), (14) and (16). Similar requirements can be derived for the other three atoms in the unit cell (A(2), B(1) and B(2)) and the final relationships are summarized in Table 2. The sign conventions in Table 2 are, as expected, consistent with those in Table 1. By using Table 2 the six anharmonic parameters can be reduced to two. The refinements in Section 4 below were actually carried out with  $|\beta_{332}| = |\beta_{332}'|$  because of the high correlation between these parameters. For convenience to those readers familiar with the notation of Mair and Barnea (1975), Table 3 contains the relationships in that notation.

It is of particular interest to note that considerable differences in the magnitudes of the  $\beta_{rst}$  parameters are predicted in Table 2, where  $\beta_{313} = 0$ . The choice of constraints between the  $\beta_{rst}$  parameters has its most pronounced effect on the predicted separation between the locations of the A and B atoms along the *c*-axis. The ratio of this distance and *c*, usually called the *u* (or *z*) parameter, is not determined by symmetry and has been included as one of the refined parameters in the analyses discussed in Section 4. The sensitivity of the *u* parameter to the model used for least-squares refinement will be discussed by Stevenson *et al.* (1982) and Stevenson and Barnea (1982) (hereafter referred to as SMB and SB respectively) for CdS and CdSe respectively.

If equation (14) is expressed in the notation of Mair and Barnea (1975) and the sign conventions of Table 3 are used the result is

$$\frac{2}{9}\sqrt{6}|\beta_1| - |\beta_2| + \frac{1}{2}|\beta_3| = 0, \quad (17)$$

which should be the same as equation (7) of Mair and Barnea (1975). The discrepancy between the two equations is due to an error made by these authors, which is rectified if the three terms in their equation are multiplied by  $a^3$ ,  $a^2c$  and  $c^3$  respectively.

#### 4. Experimental Tests

The least-squares refinement program used for the analyses discussed here calculates the correlation matrix for refined parameters in accordance with Geller (1961) and Rollett (1965). This program also calculates weights for reflection data according to a scheme in which the total variance contains contributions due to counting and population statistics, thermal diffuse scattering and extinction corrections and other sources (an inadequate weighting scheme may cause strong interactions (high correlations) between refined parameters).

Analyses of extensive X-ray data sets for CdS and CdSe will be reported by SMB and SB respectively. The analyses are carried out within Dawson's (1967*a*) structure factor formalism. Some of the results are discussed briefly here, in order to demonstrate the improvement in the structure factor model as a result of including the anharmonic temperature factors and using realistic constraints between anharmonic parameters.

Table 4 lists relevant details of the analyses for both CdS and CdSe data; no distinction was made between atomic species in assigning the magnitudes of the

anharmonic parameters. Hamilton's  $R$ -factor ratios  $R_{X+1}/R_X$  ( $X = 1$  or  $2$ ) correspond to a rejection of the appropriate hypotheses at the 0.5% significance level (Hamilton 1965), which is 'highly significant' (Hamilton 1964). The largest correlation coefficients observed are approximately 0.8 (between, for example, the extinction parameter and the scale factor). Such coefficients are not so large as to be considered unreasonable. The largest coefficient involving the anharmonic parameter is approximately 0.5 (for interaction with the  $u$  parameter).

**Table 4.** Analyses of CdS and CdSe data for three models

Harmonic temperature factors for model I:  $\beta_{313} = \beta_{332} = \beta_{337} = 0$ ; anharmonic temperature factors for model II:  $|\beta_{313}| = |\beta_{332}| = |\beta_{337}|$  (signs as in Table 1); anharmonic temperature factors for model III:  $|\beta_{313}| = 0$ ,  $|\beta_{337}| = \sqrt{2}|\beta_{332}|$  (signs as in Table 2). The numbers of independent reflections for CdS and CdSe were 118 and 270 respectively

	$\theta$ (deg.)	$\lambda$ (Å)	$T$ (K)	$R_I^A$ (%)	$R_{II}^A$ (%)	$R_{III}^A$ (%)	$GF_I^B$	$GF_{II}^B$	$GF_{III}^B$
CdS	21–65	0.7107	293(2)	1.065	0.716	0.691	1.538	1.038	1.000
CdSe	15–61	0.7107	293(2)	1.363	0.981	0.941	1.737	1.252	1.201

<sup>A</sup>  $R_X$  denotes Hamilton's  $R$  factor (Hamilton 1965) for model  $X$ .

<sup>B</sup>  $GF_X$  denotes the goodness-of-fit parameter for model  $X$ .

The introduction of anharmonicity in the structure factor model has thus resulted in much better agreement between theory and experiment. The consequences of anharmonicity in wurtzite structures have been discussed by other authors (see e.g. Whiteley *et al.* 1978). Among these consequences, the existence of intensity differences for non-symmetry related reflections occurring at the same Bragg angle is of particular interest. Such differences were observed by Whiteley *et al.* and have been observed in both studies mentioned in this section, rendering the inclusion of anharmonicity in the theoretical model mandatory. In general, the neglect of anharmonic effects in room-temperature X-ray studies requires justification.

Once the need to include anharmonic effects has been acknowledged, it is important to use a realistic model, with appropriate constraints between refinable parameters, if necessary. This is not only important if realistic anharmonic parameter values are desired but also for other parameters, in particular position parameters not determined by symmetry. This was demonstrated in the analysis of CdS data when the  $u$  parameter changed by between 8 and 9 e.s.d. (from 0.37774 to 0.37714) as a result of using model III rather than model II (see Table 4). The corresponding change in the  $u$  parameter for CdSe was between 16 and 17 e.s.d. (from 0.37661 to 0.37596), the larger change being due predominantly to a smaller e.s.d. rather than a larger absolute change. The  $u$  parameter values obtained with model I are approximately midway between those from models II and III, in each case, and approximate closely the values corresponding to the equilibrium positions of the atoms (rather than the positions defining the minima of the OPP, as is the case with models II and III).

The more extensive CdSe data set offers the opportunity of checking the degree of anisotropy of the cubic anharmonic parameters, as predicted in Table 2. This is achieved by refining special groups of reflections, for which the structure factor is independent of certain anharmonic parameters; for example structure factors for

reflections with  $l = 0$  only depend on  $\beta_{332}$ . For the  $\beta_{337}$  determination,  $\beta_{313}$  was constrained to be zero. The results gave  $|\beta_{337}/\beta_{332}| = 1.3(0.3)$ , in good agreement with the predicted value of  $\sqrt{2}$ . The somewhat large e.s.d. for  $|\beta_{337}/\beta_{332}|$  is due primarily to the e.s.d. for  $\beta_{337}$ , which reflects the interaction with the  $u$  parameter. The  $hk0$  reflections, from which  $\beta_{332}$  is determined, have structure factors which are independent of the  $u$  parameter and so no such correlation occurs in this case.

A discussion of the use of constraint relations (for anharmonic parameters), which have been derived without assuming that the structure is ideal and without using equation (13), is given in the Appendix. These relations may be of particular interest when analysing data collected from the wurtzite structures which differ most from the ideal, for example AlN, whose  $c/a$  ratio is approximately 2% different from the ideal value.

The findings of this paper for the wurtzite structure have general implications for structure analysis, especially in cases of lower symmetry where more parameters are needed to specify the model. The treatment of anharmonic thermal vibrations will, of course, be more important at elevated temperatures for both X-ray and neutron studies.

### Acknowledgments

The authors are grateful to S. L. Mair for useful discussions and also express their gratitude to the referees for their constructive criticism. One of the authors (AWS) gratefully acknowledges the financial support of a Commonwealth Post-graduate Research Award. One of the authors (ZB) thanks G. F. and J. Ling for their kind hospitality during the last stages of completion of this paper. This work was supported by the Australian Research Grants Scheme.

### References

- Bradley, C. J., and Cracknell, A. P. (1972). 'The Mathematical Theory of Symmetry in Solids' (Oxford Univ. Press).
- Dawson, B. (1967a). *Proc. R. Soc. London A* **298**, 255.
- Dawson, B. (1967b). *Proc. R. Soc. London A* **298**, 264.
- Geller, S. (1961). *Acta Crystallogr.* **14**, 1026.
- Gradshteyn, I. S., and Ryzhik, I. M. (1965). 'Tables of Integrals, Series, and Products' (Academic: New York).
- Hamilton, W. C. (1964). 'Statistics in Physical Science' (Ronald: New York).
- Hamilton, W. C. (1965). *Acta Crystallogr.* **18**, 502.
- Johnson, C. K. (1970). In 'Thermal Neutron Diffraction' (Ed. B. T. M. Willis), pp. 132–60 (Oxford Univ. Press).
- Lawaetz, P. (1972). *Phys. Rev. B* **5**, 4039.
- Mair, S. L., and Barnea, Z. (1975). *Acta Crystallogr. Sect. A* **31**, 201.
- Mair, S. L., and Wilkins, S. W. (1981). *Acta Crystallogr. Sect. A* **37**, 264.
- Moss, G. R. (1977). Ph.D. Thesis, University of Melbourne.
- Nizzoli, F. (1976). *J. Phys. C* **9**, 2977.
- Rollett, J. S. (1965). 'Computing Methods in Crystallography' (Pergamon: Oxford).
- Stevenson, A. W., and Barnea, Z. (1982). (to be published).
- Stevenson, A. W., Milanko, M., and Barnea, Z. (1982). (to be published).
- Von der Lage, F. C., and Bethe, H. A. (1947). *Phys. Rev.* **71**, 612.
- Whiteley, B., Moss, G., and Barnea, Z. (1978). *Acta Crystallogr. Sect. A* **34**, 130.



### Appendix. More General Constraint Relations

The effect of anharmonicity on the  $u$  parameter can be predicted theoretically by calculating the mean value of  $z$  for the two atoms concerned. Using the ensemble average, we get

$$\begin{aligned}\langle z \rangle &= \frac{\int z \exp\{-v(\mathbf{r})/k_B T\} d^3r}{\int \exp\{-v(\mathbf{r})/k_B T\} d^3r} \\ &\approx \frac{\int z \exp\{-v_2(\mathbf{r})/k_B T\} \{1 - v_3(\mathbf{r})/k_B T\} d^3r}{\int \exp\{-v_2(\mathbf{r})/k_B T\} \{1 - v_3(\mathbf{r})/k_B T\} d^3r},\end{aligned}\quad (\text{A1})$$

where  $v_i(\mathbf{r})$  denotes the sum of  $i$ th order terms in  $v(\mathbf{r})$ . The expression for  $\langle z \rangle$  given in equation (A1) does not depend on  $\beta_{332}$  because terms in the integrands containing  $\beta_{332}$  are all odd in at least one of the atomic displacements. Physically, this occurs because  $\beta_{332}$  is a force constant for motion in the basal plane only. The final expression for  $\langle z \rangle$  is

$$\langle z \rangle = -B_{33}\{(2B_{11} + 3B_{33})\beta_{313} - 3(B_{11} - B_{33})\beta_{337}\}/64\pi^4 k_B T. \quad (\text{A2})$$

Equation (A2) is valid for the four atoms in the unit cell and is the same for the A(1) (B(1)) and A(2) (B(2)) atoms. The use of equation (A2) for predicting the effect of anharmonicity on the  $u$  parameter, with different constraints between the anharmonic parameters, will be discussed by SMB and SB. In particular we note that if the constraints in Table 2 are substituted in equation (A2), remembering that  $B_{11} = B_{33}$  has been assumed, then  $\langle z \rangle$  is zero for all atoms. This implies that, under the assumptions made in deriving the constraints in Table 2, the refined values of the  $u$  parameter from models I and III should be approximately the same. Any sizable differences can be attributed to a breakdown of the assumptions made.

If the non-ideal nature of a wurtzite structure is to be allowed for in deriving a set of constraints between the anharmonic parameters, equation (12) cannot be used. More general relations, applicable to the A(1) atom and analogous to relations (14)–(16), are as follows:

$$\begin{aligned}48\pi^2 k_B T a c (u - \tfrac{1}{2})(B_{11}^{-1} - B_{33}^{-1}) - 2a\{3c^2(u - \tfrac{1}{2})^2 + a^2\}\beta_{313} \\ + 6\sqrt{3} a^2 c (u - \tfrac{1}{2})\beta_{332} - 3a\{12c^2(u - \tfrac{1}{2})^2 - a^2\}\beta_{337} = 0,\end{aligned}\quad (\text{A3})$$

$$\begin{aligned}16\sqrt{3} \pi^2 k_B T \{3(u - \tfrac{1}{2})^2 c^2 - a^2\}(B_{11}^{-1} - B_{33}^{-1}) \\ - 2\sqrt{3} (u - \tfrac{1}{2})c\{3(u - \tfrac{1}{2})^2 c^2 + a^2\}\beta_{313} + 6a\{6(u - \tfrac{1}{2})^2 c^2 - a^2\}\beta_{332} \\ - 3\sqrt{3} (u - \tfrac{1}{2})c\{12(u - \tfrac{1}{2})^2 c^2 - 11a^2\}\beta_{337} < 0,\end{aligned}\quad (\text{A4})$$

$$24\pi^2 k_B T (B_{11}^{-1} - B_{33}^{-1}) - 3cu\beta_{313} - 18cu\beta_{337} < 0. \quad (\text{A5})$$

If the structure is assumed to be ideal ( $c/a = \sqrt{\frac{8}{3}}$  and  $u = \frac{2}{3}$ ) and  $B_{11} = B_{33}$  is assumed, relations (A3)–(A5) reduce to (14)–(16) respectively.

Relations (A3)–(A5) do not contain sufficient information to yield suitable constraints between  $\beta_{313}$ ,  $\beta_{332}$  and  $\beta_{337}$ . However, if the value of  $|\beta_{332}|$  is determined from a refinement of  $hk0$  reflections (as described in Section 4), equation (A3) becomes sufficient (where the signs of  $\beta_{332}$  and  $\beta_{337}$  are taken to be those in Table 2). The values of the refined parameters ( $u$ ,  $B_{11}$ ,  $B_{33}$  and  $|\beta_{337}|$ ) can be substituted in inequalities (A4) and (A5) to ensure that they have been satisfied. This procedure is extended to the other atoms in the unit cell.

In an attempt to demonstrate the usefulness of this technique the extensive CdSe data set was used (since the CdS data set contains too few  $hk0$  reflections with which to determine  $\beta_{332}$ ). The final value of the  $u$  parameter was 0.37586(4), significantly different from the value obtained using model III. SB will discuss this result in greater detail. The value of Hamilton's  $R$  factor was reduced (from 0.941% for model III) to 0.937% which, although '*not significant*' (Hamilton 1964), offers some hope that these more general constraints between anharmonic parameters will be useful. This view is supported by the fact that the structure of CdSe is very close to that of ideal wurtzite, for example see the list of 20 wurtzite structures and their  $c/a$  ratios given by Lawaetz (1972).

Manuscript received 31 May, accepted 14 July 1982